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Ionic liquid azides from azidoethyl, alkyl and alkenyl substituted derivatives of 1,2,4- and 1,2,3-amino-triazoles, were prepared and examined for the first time in order to investigate their structural and physical properties. All reported salts possess melting points below 100°C. The unique character of these newly discovered ionic liquid azides is based upon the fact that these molecules are not simple protonated salts like previously reported substituted hydrazinium azides. The presence of quaternary nitrogen confers both thermal stability and negligible volatility.

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Liquid azide salts (PREPRINT)

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Abstract. Ionic liquid azides from azidoethyl, alkyl and alkenyl substituted derivatives of 1,2,4- and 1,2,3-amino-triazoles, were prepared and examined for the first time in order to investigate their structural and physical properties. All reported salts possess melting points below 100°C. The unique character of these newly discovered ionic liquid azides is based upon the fact that these molecules are not simple protonated salts like previously reported substituted hydrazinium azides. The presence of quaternary nitrogen confers both thermal stability and negligible volatility.

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Introduction.

The azide anion was discovered by Curtius in 1890.[1] Ever since, azide chemistry has fascinated generations of chemists. Covalent and ionic azides have been prepared involving almost every single element from the periodic table. Only recently, the chemistry of simple main-group and transition-metal azides have provided another high point in azide chemistry.[2-31] However, so far, azides have found only limited use because of their violent, explosive character, toxic decomposition products and the attendant danger in handling them. The lately discovered transition-metal azides are no exception to that tendency. A process for the controlled decomposition of azides would be especially valuable due to the high exothermicity of the reaction and the low molecular weight of the decomposition gases (e.g. equation 1).[32] These two characteristics make azides very valuable energetic materials.

$$H_2NNH_3^+ N_3^- \longrightarrow 2.18\ N_2 + 1.52\ H_2 + 0.65\ NH_3 \qquad (1)$$
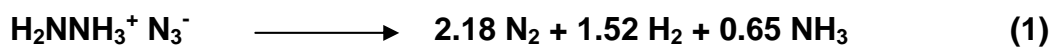
Like the azide anion, hydrazinium azide was also discovered by Curtius.[33] The usefulness of hydrazinium azide and other close related azides as energetic materials has been covered in a series of papers and patents.[34-36] Surprisingly, no comprehensive studies were reported for nearly 30 years, until Klapötke et al. investigated the structural and physical properties of hydrazinium azides in great length and detail. Unfortunately, these materials are volatile and hygroscopic.[37-44]

Two of the first compounds studied, hydrazinium azide, $[H_2NNH_3]^+[N_3]^-$, and hydrazinium azide hydrazinate, $[H_2NNH_3]^+[N_3]^-\cdot H_2NNH_2$, possess melting points of 75°C and 65°C respectively. This qualifies them as ionic liquids according to the conventional definition (i.e. a salt with a mp. $\leq$ 100°C). If Curtius would have used the term 'ionic liquid' in his time, he would be recognized as one of the progenitors of ionic liquids as we know them today. Over the last decade, ionic liquids have received much attention as replacements for common organic solvents and more recently as energetic materials because of their desirable characteristics.[45] The newly discovered ionic liquid azides described herein are unique in not being simple, protonated salts like the previously reported substituted and unsubstituted hydrazinium azides. Substitution of the hydrogens of hydrazinium azide with methyl groups leads to an increase in volatility. In addition, the undesirable and dangerous elimination of HN_3 from the molecules became more favorable.[37-44] In the compounds presented here, the presence of quaternary nitrogen confers both thermal stability and negligible volatility along with low vapor toxicity. Previously reported azides, particularly urotropinium azide,[46] permethylated hydrazinium azides[39] and 1,5-diamino-4-methyl-tetrazolium azide,[47] showed melting points exceeding the benchmark for an ionic liquid. The reported salts here possess melting points below 100°C and some are even room-temperature ionic liquids.

Experimental Section

Caution! None of the prepared triazolium azides appeared to show particular sensitivity toward friction or impact, and no accidents or mishaps occurred during this

work. However, the use of appropriate safety precautions (safety shields, face shields, leather gloves, and protective clothing such as heavy leather welding suits and ear plugs) is essential for work with energetic materials, especially when working on a larger scale. Silver azide is a well known energetic material and can explode violently under certain conditions. ***Ignoring safety precautions can lead to serious injuries!***

All chemical reagents and solvents were purchased from Aldrich Chemical Company, Inc. and their purities were checked by ^{1}H and ^{13}C NMR prior to use. The alkyl halides (allyl bromide, 1,2-dibromoethane, methyl iodide), 4-amino-1,2,4-triazole (99%), acetonitrile (99.93+% HPLC grade), methanol (99.93% A.C.S. HPLC grade), diethyl ether (anhydrous, 99+%, A.C.S. Reagent) and the azide exchange resin (azide on Amberlite® IRA-400, 16-50 mesh. ~3.8mmol N_3/g) were used as received. 2-bromoethanol was distilled with the exclusion of light and stored inside a sealed Schlenk vessel under nitrogen in the dark. 1-amino-1,2,3-triazole[48] and the triazolium halide salts[48, 49] were prepared according to literature procedures. Silver azide was prepared according to a literature procedure[42] but it was thoroughly washed with either ethanol or methanol instead of water. The silver azide was always kept suspended in alcohol and never allowed to dry! Nonvolatile solids were handled in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded in the range 4000-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. Pyrex melting point capillaries or 5mm glass NMR tubes were used as sample containers. Nuclear magnetic resonance spectra were recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield[TM] spectrometer at room temperature with each salt sample being measured as a neat liquid or dissolved in DMSO-d_6 in 5mm NMR tubes. The ^{1}H and [13]C

spectra were referenced to external samples of neat TMS; ^{14}N and ^{15}N spectra were referenced to external samples of neat nitromethane. Melting points were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 Differential Scanning Calorimeter. Measurements were carried out at a heating rate of 10°C/min in sealed aluminum pans with a nitrogen flow rate of 20mL/min. The reference sample was an empty Al container which was sealed in the nitrogen atmosphere of a glove box.

X-ray Analyses. The single crystal X-ray diffraction data were collected on a Bruker 3-circle platform diffractometer equipped with a SMART detector with the χ-axis fixed at 54.74° and using MoK$_\alpha$ radiation (λ = 0.71073 Å) from a fine-focus tube. The diffractometer was equipped with a KryoFlex apparatus for low temperatures using controlled liquid nitrogen boil off. The goniometer head, equipped with a nylon Cryoloop and magnetic base, was used to mount the crystals using perfluoropolyether oil. Cell constants were determined from 90 ten-second frames. A complete hemisphere of data was scanned on omega (0.3°) with a run time of ten-second per frame at a detector resolution of 512 x 512 pixels using the SMART software.[50, 51] A total of 2400 frames were collected in four sets and final sets of 50 frames, identical to the first 50 frames, were also collected to determine any crystal decay. The frames were then processed using the SAINT software[52, 53] to give the hkl file corrected for Lp/decay. The absorption correction was performed using the SADABS[54] program. The structures were solved by the direct method using the SHELX-90[55] program and refined by the least squares method on F^2, SHELXL-97[56] incorporated in SHELXTL Suite 5.10.[57, 58] All non-hydrogen atoms were refined anisotropically. For the anisotropic displacement parameters, the U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor.

The hydrogen atoms were located either from difference electron density maps or generated at calculated positions.

1-methyl-4-amino-1,2,4-triazolium azide (1a): To a 500mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 3.97g (17.56mmol) of 1-methyl-4-amino-1,2,4-triazolium iodide was added and dissolved in ca. 200mL of ethanol. All further handlings were carried out with the exclusion of light. 19.47mmol (2.92g) of freshly prepared silver azide was added to the stirred triazole solution. Stirring was continued for 24h. The silver iodide formed, together with excess silver azide, was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind an off-white solid. Yield: 74%; melting point (peak): +43°C; decomp. onset: +129°C. Raman (200mW, 25°C, cm^{-1}) ν = 3251(1), 3150(4), 3060(5), 3021(4), 2952(12), 2821(4), 1621(4), 1573(5), 1539(2), 1433(4), 1405(44), 1330(77), 1262(1), 1244(9), 1226(5), 1177(4), 1093(7), 1075(19), 1029(3), 984(16), 914(0+), 891(0+), 740(2), 657(1), 617(11), 455(7), 332(6), 303(6), 123(100), 102(84), 85(76); δ_{1H} (400 MHz, neat liquid at +50°C) 9.61 (1H, s, br), 8.55 (1H, s, br), 6.55 (2H, s, br, NH$_2$), 3.77(3H, s, br, CH$_3$); δ_{13C} (100 MHz, neat liquid at + 50°C) 145.5, 143.6, 39.1.

1-amino-3-methyl-1,2,3-triazolium azide (1b): Method a) To a 500mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 4.99g (22.07mmol) of 1-amino-3-methyl-1,2,3-triazolium iodide was added and dissolved in ca. 40mL of methanol. All further handlings were carried out with the exclusion of light. 30.04mmol (4.50g) of freshly prepared silver azide was added to the stirred triazole solution. Stirring was continued for 24h. The silver iodide formed, together with excess silver azide was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a

white solid. Raman and NMR spectroscopy revealed product contamination by NaN_3 which remained from the AgN_3 preparation.

Method b) To a 250mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen 1.92g (8.49mmol) 1-amino-3-methyl-1,2,3-triazolium iodide was added and dissolved in ca. 30mL of acetonitrile. 11.18g of azide exchange resin (3.8mmol N_3/g = 42.48mmol) was added to the stirred solution. Stirring was continued for 16h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a white crystalline solid. Yield 98%; melting point (peak): +50°C; decomp. onset +156°C. Raman (200mW, 25°C, cm^{-1}) ν = 3150(4), 3143(6), 3013(17), 2953(15), 2938(14), 2866(4), 2821(2), 2782(1), 1536(5), 1480(4), 1469(4), 1449(2), 1418(3), 1398(7), 1332(29), 1256(4), 1225(0+), 1199(1), 1093(13), 1049(5), 1037(3), 983(0+), 942(4), 750(2), 732(2), 635(5), 626(4), 488(6), 462(1), 452(3), 333(2), 322(3), 102(56), 84(100); δ_{1H} (400 MHz, DMSO) 8.80 (1H, s), 8.58 (1H, s), 8.49 (2H, s, NH_2), 4.23(3H, s, CH_3); δ_{13C} (100 MHz, DMSO) 131.9, 127.1, 40.05.

1-(2-hydroxyethyl)-4-amino-1,2,4-triazolium azide (2): To a 500mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 4.1264 g (19.74 mmol) of 1-hydroxyethyl-4-amino-1,2,4-triazolium bromide was added and dissolved in ca. 50ml of ethanol. All further handlings were carried out with the exclusion of light. 23.85 mmol (3.5751 g) of freshly prepared silver azide was added to the stirred triazole solution. Stirring was continued for 36h. The silver bromide formed, together with excess silver azide, was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a pale yellow liquid. Yield: 92%; glass transition: -50°C; decomp. onset: +129°C.

In a modification of the above procedure, water was used instead of methanol as a solvent. An isolated yield of the pure product, 83%, was achieved. Raman (500mW, 25°C, cm^{-1}) ν = 3147(5), 3010(6), 2961(18), 2884(8), 2731(2), 1628(2), 1563(4), 1524(4), 1465(6), 1442(6), 1409(24), 1331(36), 1247(7), 1190(4), 1161(3), 1076(16), 989(8), 947(5), 871(7), 723(4), 676(2), 630(5), 606(9), 501(5), 451(5), 347(4), 306(3), 261(7), 104(78), 84(100); δ_{1H} (400 MHz, neat liquid) 9.48 (1H, s, br), 8.45 (1H, s, br), 6.30 (2H, s, br, NH$_2$), 4.71 (1H, s, OH), 4.00 (2H, s, br, -CH_2CH$_2$OH), 3.36 (2H, s, br, -CH$_2$CH_2OH); δ_{13C} (100 MHz, neat liquid) 145.8, 143.4, 59.0, 55.5.

1-allyl-4-amino-1,2,4-triazolium azide (3a) To a 250mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 0.83g (4.08mmol) 1-allyl-4-amino-1,2,4-triazolium bromide was added and dissolved in ca. 30mL of acetonitrile. 5.19g of azide exchange resin (3.8mmol N$_3$/g = 19.72mmol) was added to the stirred solution. Stirring was continued for 16h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind an amber liquid. Yield 97%; glass transition: -57°C; decomp. onset: +109°C. Raman (500mW, 25°C, cm^{-1}) ν = 3136(5), 3121(7), 3087(11), 3023(14), 2984(15), 2942(16), 2876(2), 1647(16), 1559(4), 1519(2), 1413(13), 1328(19), 1293(8), 1247(2), 1202(0+), 1073(9), 998(4), 946(3), 920(2), 697(1), 652(2), 618(1), 573(3), 505(1), 456(2), 400(2), 289(0+), 107(48), 84(100); δ_{1H} (400 MHz, DMSO) 10.24 (1H, s), 9.22 (1H, s), 7.06 (2H, s, NH$_2$), 6.02 (1H, m, CH$_2$CH=CH$_2$), 5.38 (2H, m, CH_2CH=CH$_2$), 5.02 (2H, d, CH$_2$CH=CH_2); δ_{13C} (100 MHz, DMSO) 145.8, 143.3, 130.8, 121.4, 54.3.

1-amino-3-allyl-1,2,3-triazolium azide (3b) To a 250mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 1.83g (8.97mmol) 1-allyl-4-amino-1,2,4-

triazolium bromide was added and dissolved in ca. 30mL of acetonitrile. 12.83g of azide exchange resin (3.8mmol N_3/g = 48.75mmol) was added to the stirred solution. Stirring was continued for 16h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind an amber liquid. Yield 97%; glass transition: -62°C; decomp. onset: +114°C. Raman (500mW, 25°C, cm^{-1}) $\nu =$ 3089(8), 3027(13), 2987(14), 2948(15), 1669(3), 1646(14), 1529(4), 1420(8), 1331(24), 1295(7), 1248(3), 1219(3), 1086(5), 1052(14), 950(4), 921(2), 775(1), 754(0+), 703(4), 663(3), 634(3), 579(3), 482(2), 396(2), 84(100) ; δ_{1H} (400 MHz, DMSO) 8.85 (1H, s), 8.58 (1H, s), 8.57 (2H, s, NH_2), 6.01 (1H, m, $CH_2CH=CH_2$), 5.33 (2H, m, $CH_2CH=CH_2$), 5.22 (2H, d, $CH_2CH=CH_2$); δ_{13C} (100 MHz, DMSO) 130.9, 130.3, 127.1, 122.0, 55.2.

1-(2-bromoethyl)-4-amino-1,2,4-triazolium bromide (4) To a 500mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 9.89g (117.63mmol) 4-amino-1,2,4-triazole was added and dissolved in ca. 100mL of acetonitrile at +80°C. 20mL (232mmol) of 1,2-dibromoethane were added drop wise to the stirred solution. Stirring was continued for ca. 3h. The mixture was cooled and the precipitate was removed by filtration and dried in a dynamic vacuum. The precipitate consisted off 68.4% (based on 4-amino-1,2,4-triazole) 1,1-ethylene-bis-(4-amino-1,2,4-triazolium) dibromide. The mother liquor was transferred to a Schlenk flask and the volatiles were removed in a dynamic vacuum leaving behind a crystalline white solid. Yield of the desired product 29.9% (based on 4-amino-1,2,4-triazole); melting point: +131°C; decomp. onset: 154°C. Raman (500mW, 25°C, cm^{-1}) $\nu =$ 3176(13), 3129(15), 3110(20), 3071(12), 3012(33), 2980(32), 2958(73), 2940(77), 2833(5), 2730(4), 1564(13), 1522(9), 1424(27), 1405(22), 1376(9), 1332(10), 1309(9), 1256(10), 1200(7), 1179(7), 1129(5), 1077(16), 1044(8),

984(13), 931(11), 887(4), 869(4), 709(7), 625(5), 602(10), 561(71), 459(10), 434(8), 333(10), 283(7), 209(17), 171(16), 120(29), 85(100), 70(42); δ_{1H} (400 MHz, DMSO) 10.41 (1H, s), 9.33 (1H, s), 7.16 (2H, s, NH_2), 4.84 (1H, t, -CH_2CH_2Br), 3.99 (2H, t, CH_2CH_2Br); δ_{13C} (100 MHz, DMSO) 146.0, 143.7, 53.5, 30.4.

1-(2-azidoethyl)-4-Amino-1,2,4-triazolium azide (5). To a 500mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen, 0.51g (1.88mmol) 1-(2-bromoethyl)-4-amino-1,2,4-triazolium bromide was added and dissolved in ca. 150mL of acetonitrile. 2.95g of azide exchange resin (3.8mmol N_3/g = 11.21mmol) was added to the stirred solution. Stirring was continued for ca. 16h. The insoluble polymeric reagent was removed by filtration. The solvent was removed in a dynamic vacuum leaving behind a dark amber liquid. Yield 98%; glass transition: not observed; decomp. onset: +106°C. Raman (500mW, 25°C, cm^{-1}) $\nu = 3088(7), 2955(19), 2875(6),$ 2743(3), 2249(5), 2109(6), 1647(5), 1561(7), 1522(6), 1443(11), 1410(24), 1327(32), 1245(10), 1191(5), 1073(15), 1021(7), 983(9), 944(4), 836(7), 724(4), 675(4), 631(8), 603(9), 489(4), 447(4), 84(100); δ_{1H} (400 MHz, DMSO) 10.33 (1H s,), 9.28 (1H, s,), 7.14 (2H, s, NH_2), 4.56 (1H, t, -$CH_2CH_2N_3$), 3.92 (2H, t, $CH_2CH_2N_3$); δ_{13C} (100 MHz, DMSO) 145.9, 143.8, 51.6, 48.9.

Results and Discussion

Synthesis. The different azide salts (**1a-3b, 5**, Scheme 1) were readily prepared by silver azide metathesis. The insoluble silver azide can be used in excess assuring essentially complete conversion and can be separated together with the silver halide formed during the metathesis. This process guarantees a highly pure ionic liquid azide

product. To avoid the cumbersome handling of silver azide, an alternative route was developed employing an azide exchange resin. The exchange resin method is easier to perform, but a small amine contamination from the polymeric reagent can not be easily avoided, giving the products, especially in the case of liquids, a very distinctive, amine-like smell. ^{1}H NMR spectroscopy showed amounts of less than 2% contamination. All salts are soluble in polar solvents such as acetonitrile, methanol, and water; furthermore, they are insoluble in diethyl ether, hexane, dichloromethane, and ethyl acetate. This can be used for further purification if required. All salts were characterized by ^{1}H, ^{13}C, ^{14}N and ^{15}N NMR, Raman spectroscopy and DSC analysis, and salt **1b** was additionally characterized by single crystal X-ray analysis. For the preparation of **5,** a simple two-step route was employed (equation 2, 3). In the first step, compound **4** was prepared in reasonable yield by alkylating 4-amino-1,2,4-triazole with 1,2-dibromoethane. It was identified by Raman and NMR spectroscopy and by X-ray crystallography. In a second step, **4** was treated with an azide exchange resin yielding **5** in a straightforward manner.

Vibrational spectroscopy. Raman spectroscopy proved very useful for the qualitative analysis of these compounds. The symmetric stretch band for the azide anion, ν_s, is very prominent in the Raman spectra (e.g. Figure 1). In one instance, **1b**, some sodium azide remained from the silver azide preparation. A brief look at the ^{15}N NMR spectrum (Figure 2.) showed six signals, as expected for the compound; however, the peak at 281ppm did not show the expected amino group splitting into a triplet. By comparing the Raman spectra (Figure 3.) for sodium azide (top), the product obtained (middle), and the starting material, 1-amino-3-methyl-1,2,3-triazolium iodide (bottom), contamination by sodium azide was definitively observed. IR spectroscopy was not

suitable for differentiating between ionic liquid azide and sodium azide vibrations because, although v_{as} N_3^- is very strong in IR spectra, it is so broad that different azide anion bands completely overlap. After analyzing the Raman spectra, the peak at -278.5ppm, initially assigned to the amino-group in the ^{15}N NMR spectrum, had to be reassigned to the terminal nitrogen (N_α) belonging to sodium azide (Figure 2). The amino group peak, which is the weakest peak in the spectrum, was not well resolved. This may have been due to the fact that the concentration of the sample was not high enough and the measurement time was not sufficient. A reinvestigation employing an azide exchange resin led to a very pure **1b.** In the ionic liquid azides, the strong hydrogen-bond network seen in the X-ray crystal structure (Figure 4) and discussed below causes a shift of the v_s azide vibration to lower frequency, about 30cm^{-1} from v_s in sodium azide.[59] Raman spectroscopy is also much more sensitive, than especially ^{15}N NMR, when it comes to detecting minor impurities.

Since even minor impurities are easily detectable by Raman spectroscopy, a comparison of the Raman spectra of **4** and **5** was used to check that **4** was completely converted into **5**. Halogen-carbon vibrations are usually very intense within Raman spectra and the major contribution to the vibration at 561cm^{-1} apparently comes from C-Br vibration in the bromoethyl group. This band is entirely missing from the spectrum of **5** which indicates a quantitative exchange.

^{14}N and ^{15}N NMR Spectra. ^{15}N NMR spectroscopy is the only suitable method of accounting for all nitrogens in the compounds. The ^{14}N and ^{15}N NMR chemical shifts of the neutral and alkylated compounds are listed in Table 2 and nitrogen atoms are assigned according to Scheme 2. In the ^{14}N NMR spectra, signals for the non azide nitrogens were

either not at all or only partially observable due to line broadening. In 1-amino-1,2,3-triazoles, alkylation can take place either on the N2 or N3 position. To determine the site of alkylation, a study of the ^{15}N protonation-induced shift (PIS), here actually alkylation-induced, has been a useful method in the past.[47, 60] It has been found that the protonated/alkylated nitrogen is marked by the greatest PIS. For this purpose the ^{14}N and ^{15}N data for 1-amino-1,2,3-triazole were recorded and comparison with the corresponding 4-amino-1,2,4-triazoles clearly indicates on which nitrogen alkylation occurs. The largest PIS is observed for the N3 nitrogen in the alkylated 4-amino-1,2,4-triazolium azides and is negative (~ 100ppm upfield shift). In 1-amino-1,2,3-triazoles, **1b** and **3b**, alkylation takes place at the N3 positions which show the largest PIS of -128.8ppm and -118.3ppm, respectively. The PIS for the amino groups is positive, which is in agreement with the effects observed by other groups.[47, 60]

Crystal structures of 1-amino-3-methyl-1,2,3-triazolium azide (1b) and 1-bromoethyl-4-amino-1,2,4-triazolium bromide (4). 1b crystallized in the centrosymmteric monoclinic space group, *P*2/*c*. The asymmetric unit contains two ion pairs, one of which suffers from substantial disorder in the cation as well as the azide anion (Figure 4). Even the ordered triazolium cation shows a rotational disorder in the methyl group, and two rotational conformers could be refined with a ~70:30 population. In the other cation, the 1,2,3-triazole ring is disordered with the central nitrogen N(9), sitting on a special mirror plane. This plane bisects the triazole ring and the pendant amino and methyl group are forced to occupy the same site (Figure 4, right). To complicate matters further, the methyl groups show rotational disorder. Final structure solution was accomplished by moving N(9) off the mirror plane and refining with carbon

and nitrogen atoms occupying the same site. Also, the occupancy of hydrogen atoms belonging to the amino group was set at half, while that of the six-disordered methyl hydrogens were set at a quarter, bringing the total occupancy for amino and methyl hydrogens for a symmetry generated structure (1-x, 1-y, -z) to five.   The central nitrogen N(11) in one of the azide anions also sits on a crystallographic mirror plane, which generates N(12A) with the symmetry operation 1-x, 1-y, -z.   The two crystallographically independent cationic triazole rings are nearly planar and are arranged almost perpendicular to each other, with a mean plane angle of 88.6°. Hydrogen bonding between the individual azide anions and different cations is especially pronounced. All contacts lie within the sum of the van der Waals radii of 2.75Å.[61] The ordered azide anion forms a three dimensional network with the disordered triazole ring via multiple contacts between the disordered methyl/amino site and the terminal N(12) nitrogen with distances, ranging between 2.01(2)Å and 2.57(2)Å. Lack of disorder in the cation formed by C(1), C(2), N(1), N(2) and N(3) gives a much clearer picture of the hydrogen bonding network with the disordered azide anion N(5), N(6) and N(7). The two amino protons, H(44A) and H(44B), are hydrogen-bonded to the terminal nitrogen atoms of the azide forming chains that travel along the *b*-axis. The shortest contacts are, N(4)-H(44A)···N(6A), 2.01(2)Å and N(4)-H(44A)···N(6B), 2.06(2)Å (generated using 2-x,-1+y,1/2-z symmetry). The other two significantly strong hydrogen bonds arise from N(4)-H(44B)···N(7A), 2.17(2)Å and N(4)-H(44A)···N(7B), 2.12(2)Å. Interestingly, these form an intertwined pair of helixes which run parallel to the b-axis and are ~3.8 Å apart.

4 crystallized in a monoclinic space group. Figure 5 shows the asymmetric unit and the packing arrangement along the *b* axis. The overall packing is dominated by attractive

Coulomb forces accompanied by substantial hydrogen bonding involving hydrogens from the amino group, the triazole ring, and from the bromoethyl group to the bromide anion forming a three dimensional network. It is a rather simple packed structure with alternating anions and cations. The triazole ring shows no abnormalities within the lengths and angles.[49] The ring is planar with the attached exocyclic nitrogen atom N(4) and C(3) atom from the bromoethyl group lying within the plane (the maximum torsion angle of N(4) from this plane is 1.9(2)° and 1.7(2)° for C3, respectively). The amino group is pyramidal and staggered with respect to C(2) which has been frequently observed in other structures.[47-49, 62] The pendant alkyl group is curved by C(4)-C(3)-N(1), 112.4(2)° and C(3)-C(4)-Br(2), 111.6(2)° with the bromine atom pointing back to the ring, but being dihedral twisted outward from the plane by 71.0(3)°. The bromide anion shows extensive hydrogen bonding with different cations, giving it a coordination number of seven (Figure 5.). Connections range from a very strong Br(1)···H(3) amino group bond with 2.58(4)Å to a relatively weak Br(1)···H(6) alkyl group bond of 2.99(3)Å, just below the $\Sigma_{van\ der\ Waals}$ radii of 3.05 Å.[61]

Thermal stability and sensitivity investigations and heat of formation calculations.
Phase transition and thermal decomposition temperatures were determined by DSC analysis (Table 3). For energetic materials key features are thermal stability and physical properties. In this case the ultimate goal was preparing room temperature ionic liquid azides with a long liquid range. The azide anion offers a rich platform for hydrogen bonding through both terminal nitrogen atoms, as it is evident in the crystal structure of **1b**. Therefore, the discovery of relatively low-melting azide salts could not have been

predicted from the beginning. Introducing allyl-, hydroxyethyl- and azidoethyl-

functionalities clearly promoted liquefying the ionic system. The drawback of more

energetic side chain functionalities is reflected in lower decomposition onsets for **3a**, **3b**

and **5**.

Initial safety studies were carried out with the amino-triazolium azides. Impact

testing was carried out on an Olin Mathieson style drop weight tester where a small

sample (20 mg) was placed in a steel cup and a two-kilogram mass was dropped

vertically upon a closed sample.[63] The minimum drop height in centimeters was recorded

for five consecutive negative tests. A five microgram sample of 1,3,5,7-tetranitro-1,3,5,7-

tetraazacyclooctane (HMX) was used as a standard and has a value of 34 kg cm. For

friction testing, a Julius Peters-style friction tester was employed whereby a small amount

of sample (20 mg) was placed on a small ceramic square plate and a steel pin was pushed

across the sample under a known load. Any evidence of discoloration, odor, smoke, or

spark was considered a positive test. Generally, the salts are less sensitive to impact than

RDX (Table 4). The relative insensitivity of these ionic liquid azides can be justified by

the nominally linear azide anions which exhibit symmetric N=N double bonds in contrast

to an unsymetrical N-N single and triple bonds arrangement found in covalent azides

which are notorious explosives.

Another key feature is the heat of formation of the compounds. Theoretical

performance can be estimated from calculated heats of formation. In general, a

promising compound should possess a high positive heat of formation hopefully without

inducing thermal instability or shock sensitivity. Table 3 lists the calculated heats of

formation for the compounds investigated. With one exception gas-phase heats of

formation for all the separate ions of the compounds in Table 3 were calculated by the G2 method[64] using Gaussian 98[65]. For the cation of **5**, this value was derived from the homodesmic[66] reaction of equation 4 and MP2/6-31G(d)//HF/6-31G(d) enthalpies[67] from GAMESS.[68] The sum of the enthalpies of the ions was then corrected by the lattice enthalpy of the solid as estimated using the procedures described by Jenkins[69] with the individual crystal ion volumes approximated by the volumes enclosed by the 0.001 electron contour of the HF/6-31G(d) electron density in the isolated species.

Conclusion. It has been demonstrated that true room-temperature ionic liquid azides can be obtained. The azide anion did not cause the compounds to become too sensitive to work with and an alternative preparative route has been described avoiding the handling of silver azide. This would seem to indicate that these new, less volatile, less sensitive, liquid azides may hold great potential as energetic materials.

Supporting Information Available. Crystallographic data for **1b** and **4** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature.

[1] Curtius, T. *Ber. Dtsch. Chem. Ges.* **1890**, *23*, 3023.

[2] Haiges, R.; Boatz, J.A.; Yousufuddin, M.; Christe K.O. *Angew. Chem. Int. Ed.* **2007**, *46*, 2869.

[3] Haiges, R.; Boatz, J.A.; Schroer, T.; Yousufuddin, M.; Christe, K.O. *Angew. Chem. Int. Ed.* **2006**, *45*, 4830.

[4] Klapötke, T.M.; Krumm, B.; Mayer, P.; Scherr, M. *Z. Naturforsch., B: Chem. Sci.* **2006**, *61*, 528.

[5] Haiges, R.; Schroer, T.; Yousufuddin, M.; Christe, K.O. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2691.

[6] Klapötke, T.M.; Krumm, B.; Galvez-Ruiz, J.-C.; Nöth, H. *Inorg. Chem.* **2005,** *44*, 9625.

[7] Haiges, R.; Boatz, J.A.; Bau, R.; Schneider, S.; Schroer, T.; Yousufuddin, M.; Christe, K.O. *Angew. Chem. Int. Ed.* **2005,** *44,* 1860.

[8] Haiges, R.; Boatz, J.A.; Vij, A.; Vij, V.; Gerken, M.; Schneider, S.; Schroer, T.; Yousufuddin, M.; Christe, K.O. *Angew. Chem. Int. Ed.* **2004,** *43,* 6676.

[9] Klapötke, T.M.; Krumm, B.; Polborn, K.; Schwab, I. *J. Chem. Am. Soc.* **2004**, *126*, 14166.

[10] Klapötke, T.M.; Krumm, B.; Mayer, P.; Naumann, D.; Schwab, I. *J. Fluorine Chem.* **2004**, *125*, 997.

[11] Haiges, R.; Boatz, J.A.; Schneider, S.; Schroer, T.; Yousufuddin, M.; Christe, K.O. *Angew. Chem. Int. Ed.* **2004,** *43*, 3148.

[12] Haiges, R.; Vij, A.; Boatz, J.A.; Schneider, S.; Schroer, T.; Gerken, M.; Christe, K.O. *Chem.—Eur. J.* **2004,** *10,* 508.

[13] Haiges, R.; Boatz, J.A.; Vij, A.; Gerken, M.; Schneider, S.; Schroer, T.; Christe, K.O. *Angew. Chem. Int. Ed.* **2003**, *42*, 5847.

[14] Klapötke, T.M.; Krumm, B.; Mayer, P.; Schwab, I. *Angew. Chem. Int. Ed.* **2003**, *42*, 5843.

[15] Klapötke, T.M.; Noeth, H.; Schütt, T.; Suter, M. *Eur. J. Inorg. Chem.* **2002**, 2511.

[16] Klapötke, T.M.; Krumm, B.; Mayer, P.; Piotrowski, H.; Polborn, K.; Schwab, I. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1831.

[17] Klapötke, T.M.; Krumm, B.; Mayer, P.; Piotrowski, H.; Ruscitti, O.P.; Schiller, A. *Inorg. Chem.* **2002**, *41*, 1184.

[18] Karaghiosoff, K.; Klapötke, T.M.; Krumm, B.; Nöth, H.; Schütt, T.; Suter, M. *Inorg. Chem.* **2002**, *41*, 170.

[19] Beck, W.; Fehlhammer, W.P.; Feldl, K.; Klapötke, T.M.; Kramer, G.; Mayer, P.; Piotrowski, H.; Pollmann, P.; Ponikwar, W.; Schütt, T.; Schuierer, E.; Vogt, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1751.

[20] Beck, W.; Klapötke, T.M.; Klufers, P. Kramer, G.; Rienacker, C.M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1669.

[21] Klapötke, T.M.; Schütt, T. *J. Fluorine Chem.* **2001**, *109*, 151.

[22] Klapötke, T.M.; Nöth, H.; Schütt, T.; Warchhold, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 81.

[23] Klapötke, T.M.; Krumm, B.; Mayer, P.; Ruscitti, O.P. *Inorg Chem.* **2000**, *39*, 5426.

[24] Klapötke, T.M.; Nöth, H.; Schütt, T.; Warchhold, M. *Angew. Chem. Int. Ed.* **2000**, *39*, 2108.

[25] Klapötke, T.M.; Schütt, T. *Main Group Met. Chem.* **1999**, *22*, 357.

[26] Beck, W.; Klapötke, T.M.; Knizek, J.; Nöth, H.; Schütt, T. *Eur. J. Inorg. Chem.* **1999**, 523.

[27] Klapötke, T.M.; Schulz, A. *Main Group Met. Chem.* **1997**, *20*, 325.

[28] Klapötke, T.M.; Schulz, A. *Inorg. Chem.* **1996**, *35*, 4995.

[29] Klapötke, T.M.; Geissler, P. *Dalton Trans.* **1995**, 3365.

[30] Geissler, P.; Klapötke, T.M.; Kroth, H.-J.; *Spectrochim. Acta, Part A* **1995**, *51A*, 1075.

[31] Johnson, J.P.; MacLean, G.K.; Passmore, J.; White, P.S. *Can. J. Chem.* **1989**, *67*, 1687.

[32] Kirpichev, E.P.; Alekseev, A.P.; Rubtsov, Y.I.; Manelis, G.B. *Russ. J. Phys. Chem.* **1973**, *47*, 1654.

[33] Curtius, T. *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 3341.

[34] Schieler, L. *Low Thrust Devices/Velocity Control, Semiannual Tech. Rept. 6pp.* **Jun 1961**, AD-264852.

[35] Seaman, T.F.; Kahrs, J.; Huson, G.R. *J. Spacecr. Rockets* **1971**, *8*, 1080.

[36] Koch, J.H. Pat. **1961** GE1117015, **1962** US 3066479, **1963** UK920518.

[37] Hammerl, A.; Holl, G.; Kaiser, M.; Klapötke, T.M.; Kränzle, R.; Vogt, W. *Z. Anorg. Allg. Chem.* **2002**, *628*, 322.

[38] Hammerl, A.; Holl, G.; Kaiser, M.; Klapötke, T.M.; Mayer, P., Nöth, H.; Warchhold, M. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1477.

[39] Hammerl, A.; Holl, G.; Hübler, K.; Klapötke, T.M.; Mayer, P. *Eur. J. Inorg. Chem.* **2001**, 755.

[40] Hammerl, A.; Klapötke, T.M.; Piotrowski, H. *Propellants, Explos., Pyrotech.* **2001**, *26*, 161.

[41] Habereder, T., Hammerl, A.; Holl, G. Klapötke, T.M.; Mayer, P.; Nöth, H. *Int. Annu. Conf. ICT* **2000**, *31st*, 150.

[42] Habereder, T., Hammerl, A.; Holl, G. Klapötke, T.M.; Knizek, J.; Nöth, H., *Eur. J. Inorg. Chem.* **1999**, 849.

[43] Klapötke, T.M.; White, P.S.; Tornieporth-Oetting, I.C. *Polyhedron* **1996**, *15*, 2579.

[44] Holfter, H.; Klapötke, T.M.; Schulz, A. *Eur. J. Solid State Inorg. Chem.* **1996**, *33*, 855.

[45] Singh, R.P.; Verma, R.D.; Meshri, D.T.; Shreeve, J.M. *Angew. Chem. Int. Ed.* **2006**, *45*, 3584.

[46] Ang, H.-G.; Fraenk, W.; Karaghiosoff, K.; Klapötke, T.M.; Nöth, H.; Sprott, J.; Suter, M.; Vogt, M.; Warhhold, M. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2901.

[47] Gálvez-Ruiz, J.C.; Holl, G. Karaghiosoff, K.; Klapötke, T.M.; Löhnwitz, K.; Mayer, P.; Nöth, H.; Polborn, K.; Rohbogner, C.J.; Suter, M.; Weigand, J.J. *Inorg. Chem.* **2005**, *44*, 4237.

[48] Kaplan, G.; Drake, G.; Tollison, K.; Hall, L.; Hawkins, T. *J. Heterocyclic Chem.* **2005**, *42*, 19.

[49] Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Vij, A.; Sobaski, S. *ACS Symposium Series* **2005**, *902*, 259.

[50] *SMART* V 4.045 Software for the CCD Detector System, Bruker AXS, Madison, WI, USA **1999**.

[51] *SMART* for WNT/2000, Version 5.625, Bruker AXS, Inc., Madison, WI, USA **2001**.

[52] *SAINT* V 4.035 Software for the CCD Detector System, Bruker AXS, Madison, WI, USA **1999**.

[53] *SAINT PLUS*, Version 6.22, Bruker AXS, Inc., Madison, WI, USA **2001**.

[54] *SADABS*, Program for Absorption Correction for Area Detectors, Version 2.01, Bruker AXS, Madison, WI, USA **2000**.

[55] G. M. Sheldrick, *SHELXS-90*, Program for the Solution of Crystal Structure, University of Göttingen, Germany, **1990**.

[56] G. M Sheldrick, *SHELXL-97*, Program for the Refinement of Crystal Structure, University of Göttingen, Germany, **1997**.

[57] *SHELXTL* 5.10 for Windows NT, Program Library for Structure Solution and Molecular Graphics, Bruker AXS, Madison, WI, **2000**.

[58] *SHELXTL*, Version 6.10, Bruker AXS, Inc., Madison, WI, **2000**.

[59] Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsspektroskopie: e. Einf.*, 2. Auflage; 1988.

[60] Claramunt, R.M.; Sanz, D.; Catalán, J.; Fabero, F.; García, N.A.; Foces-Foces, M.C.; Llamas-Saiz, A.; Elguero, J. *J. Chem. Soc. Perkin Trans. 2* **1993**, 1687.

[61] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

[62] Foces-Foces, M.C.; Cano, F.H.; Claramunt, R.M.; Sanz, D.; Catalán, J.; Fabero, F.; Fruchier, A.; Elguero, J. *J. Chem. Soc. Perkin Trans. 2* **1990**, 237.

[63] Test methods according to the *UN Recommendations on the Transport of Dangerous Goods,* Test 3, Third Edition, United Nations, New York and Geneva, 1999.

[64] Curtiss, L.A.; Raghavachari, K.; Trucks, G.W.; Pople, J.A. *J. Chem. Phys.*, *94*, **1991**, 7221.

[65] Frisch, M.J.; et al. GAUSSIAN98, Gaussian, Inc., Pittsburgh, PA, 1998.

[66] George, P.; Trachtman, M.; Brett, A.M.; Bock, C.W. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1036.

[67] Van Wazer, J.R.; Kellö, V.; Hess, Jr., B.A.; Ewig, C.S. *J. Phys Chem.*, *94*, **1990**, 5694.

[68] Gordon, M.S.; Schmidt, M.W. *Theory and Applications of Computational Chemistry*, edited by Dykstra, C.E.; Frenking, G.; Kim, K.S.; Scuseria, G.E. Elsevier, Amsterdam, 2005.

[69] Jenkins, H.D.B.; Tudela, D.; Glasser, L. *Inorg. Chem.*, *41*, **2002**, 2364.

Table 1. ^{15}N, ^{14}N NMR Chemical Shifts (ppm), Coupling Constants (J, Hz), ^{14}N half width ($\Delta_{1/2}$, Hz) for the compounds studied.[f, g]

compd		N1	N2	N3	N4	Nα'	Nβ'	Nγ'	Nα	Nβ
4AT[61]	$^{15}N^c$	-198.2	-66.1	-66.1	-315.5					
1AT[h]	$^{15}N^a$	-129.3	-39.7	-22.8	-300.6 $^1J(69)$					
	$^{14}N^a$	-128 $\Delta_{1/2}$ (700)	d	-23 $\Delta_{1/2}$ (1600)	-313 $\Delta_{1/2}$ (2000)					
1a	$^{15}N^a$	-187.8 (10.4)	-86.5(-20.4)	-169.3(-103.2)	-303.9(11.6) $^1J(70)$				-277.3	-132.8
	$^{14}N^b$	-190 $\Delta_{1/2}$ (350)	-85 $\Delta_{1/2}$ (800)	-170 $\Delta_{1/2}$ (200)	n.o.[d]				-283 $\Delta_{1/2}$ (150)	-133 $\Delta_{1/2}$ (45)
1b	$^{15}N^c$	-119.2(10.1)	-48.2(-8.5)	-151.6(-128.8)	-284.6(16.0) $^1J (73)$				-278.5	-133.2
	$^{14}N^c$	d	e	~-140 $\Delta_{1/2}$ (1700)	e				-276 $\Delta_{1/2}$ (200)	-132 $\Delta_{1/2}$ (70)
2	$^{15}N^a$	-189.2(9.0)	-89.7(-23.6)	-164.0(-97.9)	-306.1(9.4) $^1J (72)$				-279.6	-134.7
	$^{14}N^b$	-188 $\Delta_{1/2}$ (500)	e	-161 $\Delta_{1/2}$ (300)	e				-283 $\Delta_{1/2}$ (200)	-133 $\Delta_{1/2}$ (60)
3a	$^{15}N^a$	-187.2(11.0)	-87.6-21.5)	-160.9(-94.8)	-301.3 $^1J(71)$				-276.1	-132.0
	$^{14}N^c$	e	e	e	e				-277 $\Delta_{1/2}$ (40)	-131 $\Delta_{1/2}$ (75)
3b	$^{15}N^c$	-121.0(8.3)	-47.4(-7.7)	-141.4(-118.3)	-283.4(17.2) $^1J (64)$				-277.6	-133.4
	$^{14}N^c$	e	e	e	e				-279 $\Delta_{1/2}$ (800)	-134 $\Delta_{1/2}$ (400)
5	$^{15}N^c$	-187.8(10.4)	-89.5(-23.4)	-166.0(-99.9)	-305.0(10.5) $^1J (73)$	-172.0	-132.1	-319.1	-277.2	-134.9
	$^{14}N^c$	d	e	-170 $\Delta_{1/2}$ (700)	e	e	-133 $\Delta_{1/2}$ (140)	d	-276 $\Delta_{1/2}$ (130)	-132 $\Delta_{1/2}$ (30)

[a]neat liquid; [b]d_4-MeOH solution; [c]DMSO solution; [d]overlapping with N3; [e]not observed; [f]PIS effect in parentheses; [g]shifts were referenced to an external sample of neat CH_3NO_2; [h]this work.

Table 2. Crystal and structure refinement data for **1b** and **4**.

Compound	1b	4
Formula	$C_3H_7N_7$	$C_4H_8BrN_4$, Br
Space group	P2/c monoclinic	P21/n monoclinic
a (Å)	11.453(3)	11.531(2)
b (Å)	5.531(1)	5.540(1)
c (Å)	15.252(4)	13.941(2)
β (°)	95.385(4)	106.231(2)
V/Å^3	961.9(4)	855.1(2)
$\rho_{calc.}$/g cm^{-3}	1.462	2.112
Z	6	4
Formula weight	141.16	271.94
μ/mm^{-1}	0.110	9.416
Temperature (K)	173	173
λ(MoKα)	0.71073	0.71073
Crystal size	0.97x0.21x0.12	0.67x0.04x0.01
Reflection collected	9035	9604
Independent [R(int)]/	1762 [0.025]	2057 [0.05]
Obs. refl. ([I > 2.0 σ(I)])	1620	1805
F(000)	444	520
GooF (S)	1.07	1.06
R_1, wR [I > 2σ(I)]	0.0326, 0.0928	0.0288, 0.0688
R_1, wR_2 (all data)	0.0350, 0.0951	0.0341, 0.0711
L.diff. peak/hole eÅ^3	0.23 and -0.20	0.75 and -0.39
Absorption correct.	none	SADABS
no. parameters	185	123
Refinement method	Full-matrix least squares on F^2	

$w = 1/[\sigma^2(F_o^2)+(0.0575P)^2+0.2056P]$ where $P=(F_o^2+2F_c^2)/3$

$R_1 = \Sigma ||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma(w(|F_o|^2)^2]\}^{1/2}$

Table 3. Thermal properties of triazolium azides.

azide	$T_{g(peak)}$ (°C)	$T_{m(peak)}$ (°C)	$T_{dec(onset)}$ (°C)	$\Delta_f H^\circ_{calc.}$ (kcal mol^{-1})[b]
1a		+43	+129	+136
1b		+50	+156	+149
2	-50		+129	+93
3a	-57		+109	+161
3b	-62		+114	+173
5	[a]		+106	+223

[a]not observed; [b]for solid phase

Table 4. Initial safety test results for triazolium ionic liquid azides.[a]

azide	impact[a]	friction[b] (N)
	drop height (kg cm)	
1a	>200	>360
1b	>200	>360
2	176	353
3a	132	[c]n.d.
3b	<60	n.d.
5	>150<200	n.d.

[a]Insensitve >200kgcm, sensitive ≥40kgcm
[b]Insensitive >360N, sensitive <360N and > 80N.
[c]n.d. = not determined

Figure 1.

Figure 2.
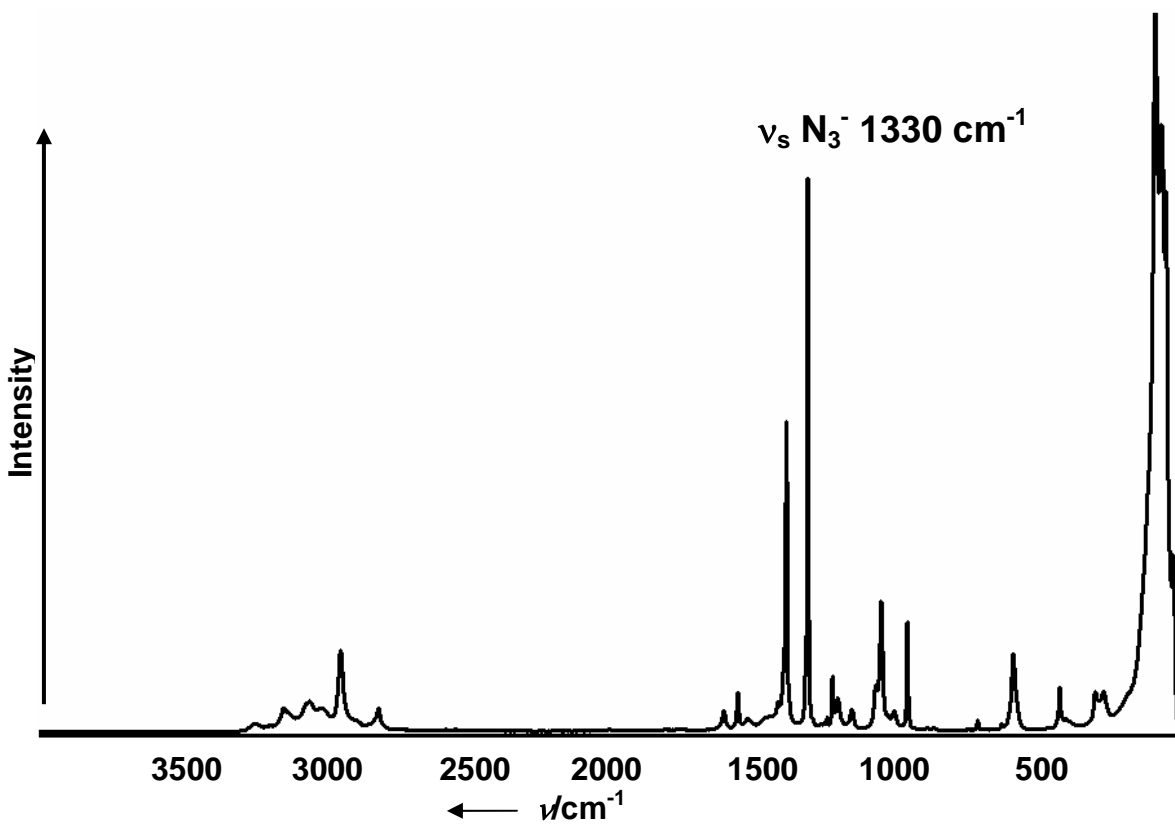
$N_{2} - 48.2$ $N_{1} -119.2$ $N_{\beta} -133.2$ $N_{3} -151.6$ $N_{\alpha} -278.5$ $N_{\alpha(NaN3)} -281.2$
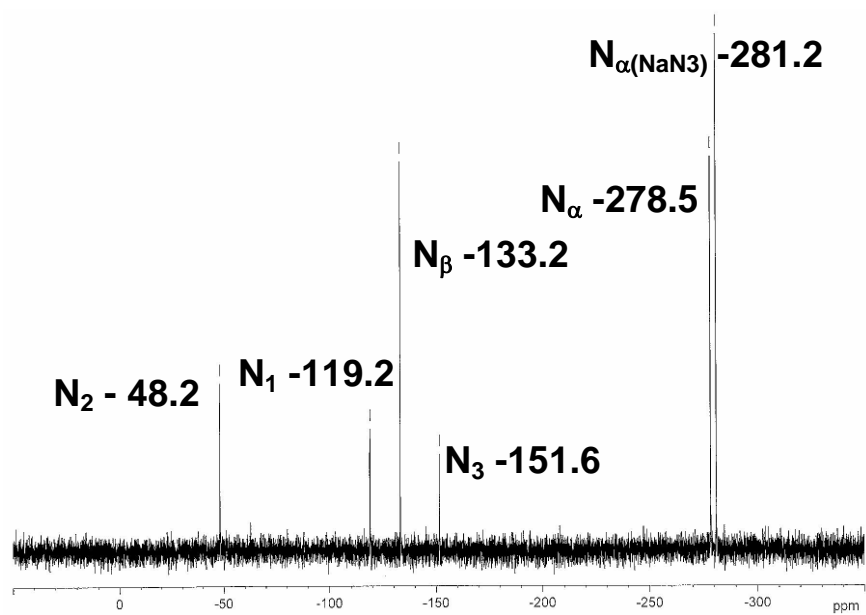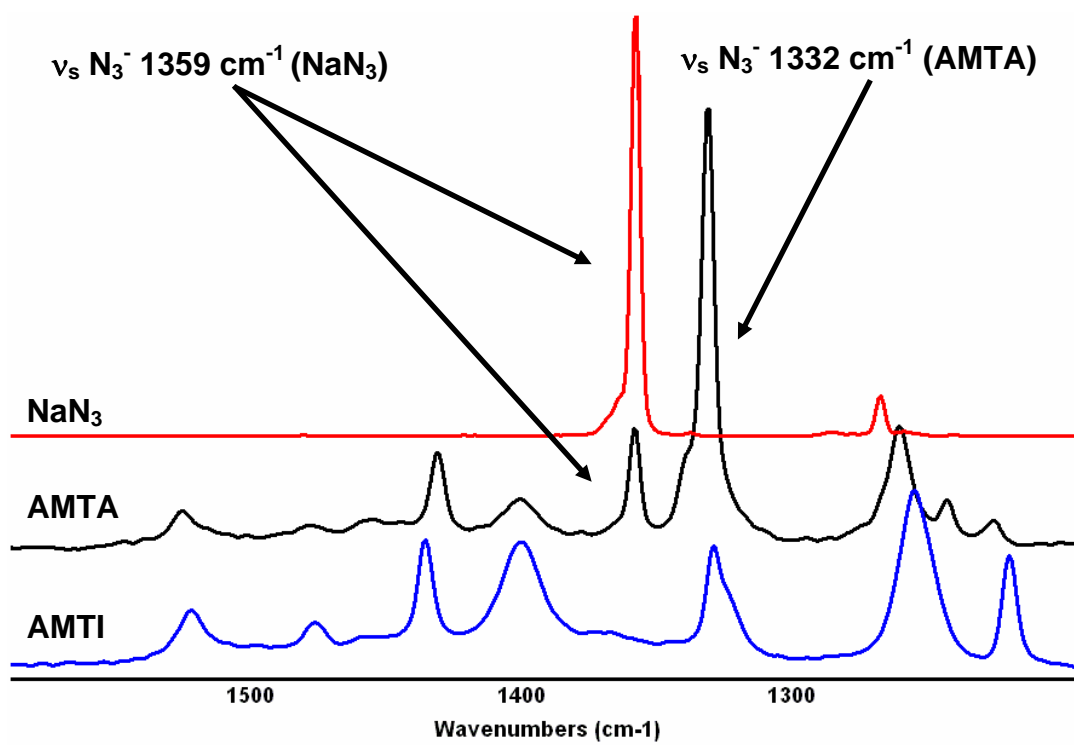
Figure 3.

Figure 4.

Figure 5.

Scheme 1.

R = CH$_3$(1), CH$_2$CH$_2$OH(2), CH$_2$CH=CH$_2$(3),

CH$_2$CH$_2$Br(4), CH$_2$CH$_2$N$_3$(5)

Equation 2, 3.

Scheme 2

R = CH$_3$(1), CH$_2$CH$_2$OH(2), CH$_2$CH=CH$_2$(3),

CH$_2$CH$_2$Br(4), CH$_2$CH$_2$N$^{\ominus}$—N$^{\oplus}$≡N(5)
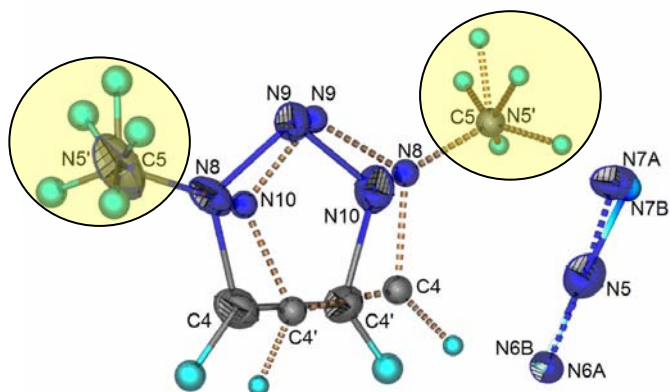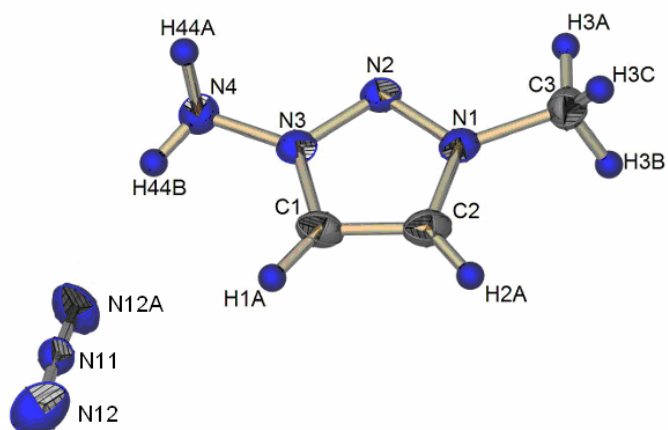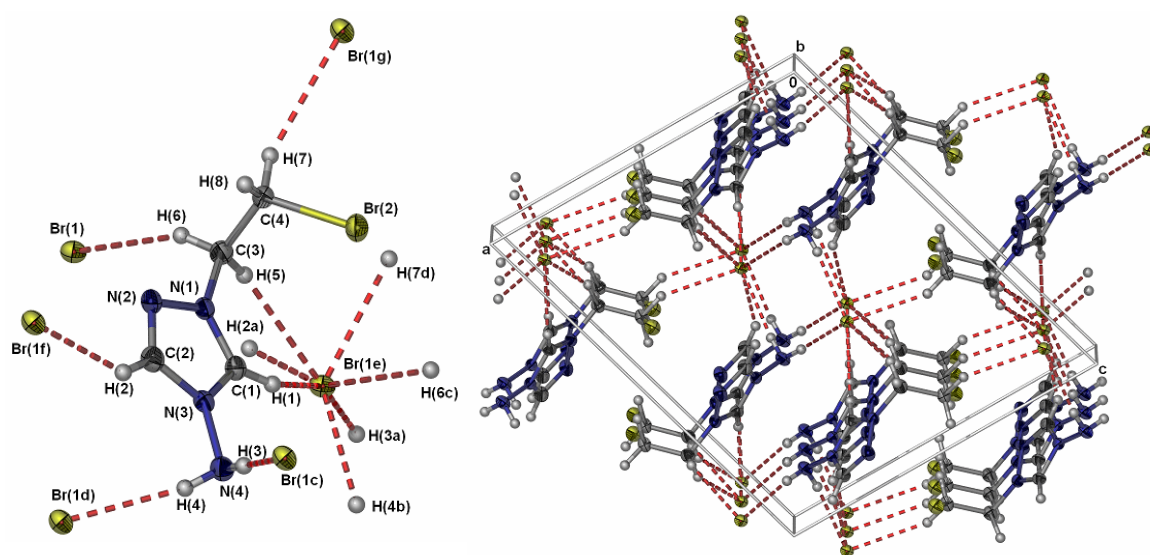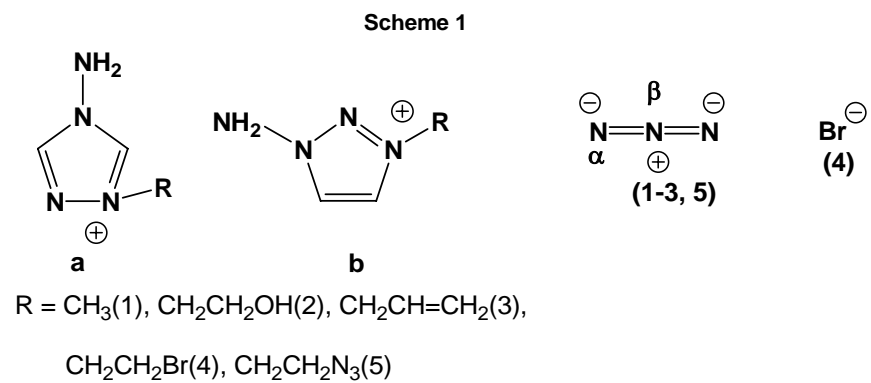
Equation 4.
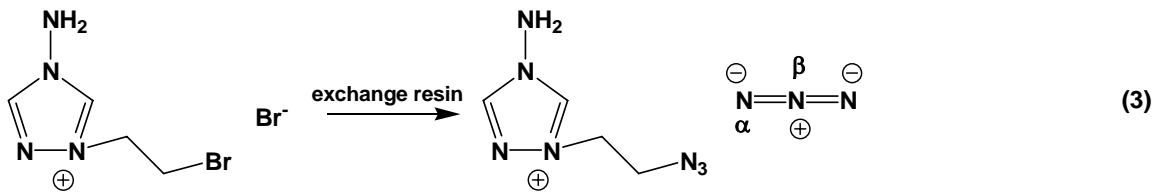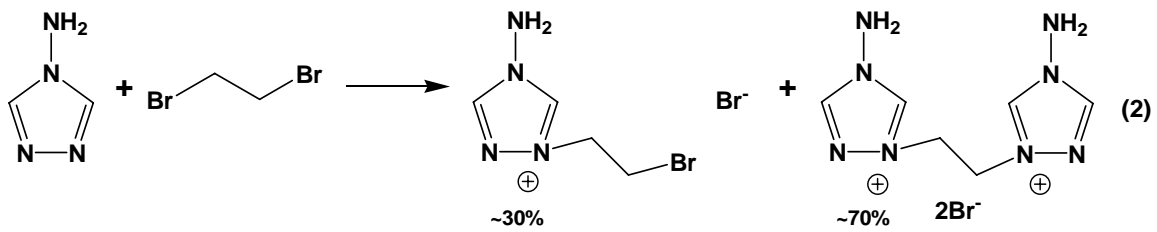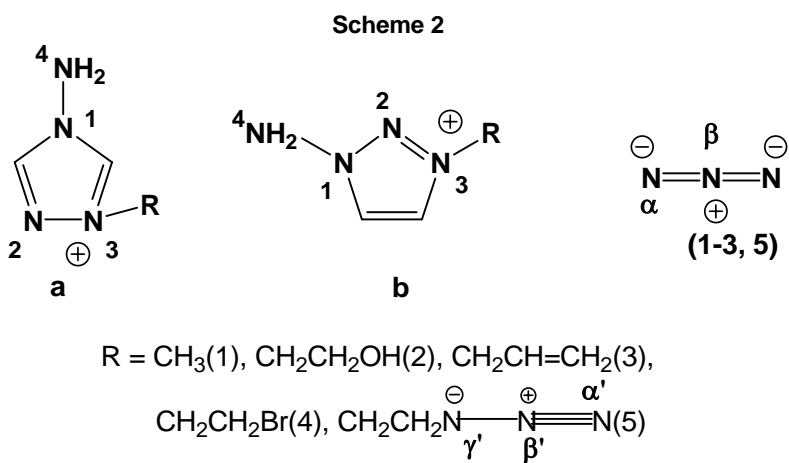
$$+ \ H_3CNH_2 + H_3CCH_3 \longrightarrow \quad + H_3CCH_2NH_2 + \ H_3CCH_2N_3 \quad (4)$$
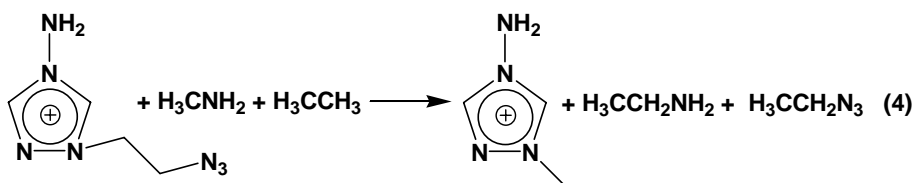
Figure captions

Figure 1. Raman spectrum of 1-methyl-4-amino-1,2,4-triazolium azide (**1**).

Figure 2. ^{15}N NMR of 1-amino-3-methyl-1,2,3-triazolium azide (d_6-DMSO) showing NaN$_3$ impurity.

Figure 3. Raman spectra of sodium azide (top), 1-amino-3-methyl-1,2,3-triazolium azide (middle), containing sodium azide as an impurity and 1-amino-3-methyl-1,2,3-triazolium iodide (bottom).

Figure 4. ORTEP diagram showing the conformation and the atom numbering scheme of the ordered triazolium azide (left, rotational disorder of the methyl group not shown for clarity) and the disordered triazolium azide with mixed C/N occupancy (right) of 1-amino-3-methyl-1,2,3-triazolium azide (**1b**).

Figure 5. ORTEP diagram showing the conformation and the atom numbering scheme of the individual cations and anions (left) and the packing diagram of 1-(2-bromoethyl)-4-amino-1,2,4-triazolium bromide (**4**) along the *b* axis (right).

Liquid azide salts

Stefan Schneider[*], Tommy Hawkins, Michael Rosander, Jeffrey Mills, Adam Brand, Leslie Hudgens, Greg Warmoth, Ashwani Vij

The first azides were discovered by Curtius in 1890 and have a well-deserved reputation for explosive behavior. Less sensitive ionic azides with good thermal stabilities would have great potential as high energy density materials. Therefore, we here investigated the synthesis of ionic liquid azides based on substituted triazolium cations. These new ionic liquids are unique in that they are not simple, protonated salts. The presence of quaternary nitrogen seems to confer both thermal stability and negligible volatility.